PHOTOCATALYTIC AND PHOTOSYNTHETIC PROCESSES WITH SEMICONDUCTOR PARTICULATES

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1. INTRODUCTION

Photochemical energy conversion by semiconductor particles suspended in a liquid has been the focus of increased interest in the last few years.[1-3] Onde of the most active area of research involves the production of fuels from inexpensive and abundant materials. Prominent among the desirable reactions are the reduction of water to hydrogen, the reduction of CO_2 and N_2, and the cleavage of H_2S.[1-6] Moreover, possible applications of the photocatalytic processes to sensitize organic transformations, such as functional group modification, have been developed and represent a new and promising area of organic photochemistry.[7, 8] Also, to the extent that some of the organic compounds are present as undesirable products in stream wastes, the possibility of utilizing photocatalytic processes in environmental control and abatement has also been exploited recently by us and others.[9, 10]

The present review article reports on recent advances in these research areas of photocatalytic processes.

2. SEMICONDUCTOR DISPERSIONS

The principles of photo-electrochemical cells have been reviewd extensively[11, 12] and can be used as a starting point in the understanding of the processes occurring at particulate suspensions; however, differences between a semiconductor electrode and semiconductor particles have to be considered.[12-15]

Photoexcitation of a semiconductor with light of energy higher than the bandgap promotes an electron from the valence band to the conduction band leaving an electron deficiency (hole) in the valence band. These electrons and holes in a particle (where no ohmic contact allows to extract the majority carriers and transfer to a second electrode, such as in the photo-electrochemical cells) move rapidly to the semiconductor/electrolyte interface and react with absorbed species or with species in solution (or alternatively, they can recombine). The energy level of the bottom of the conduction band can be considered as a measure of the reduction strenght of the photoexcited electrons, where as that of the upper position of the valence band is a measure of the oxidation strenght of the holes. Figure 1 illustrates the position of the valence and conduction bands of various semiconductors in contact with an aqueous electrolyte solution at pH 1, and compares them to the standard potentials of some redox couples.

Inasmuch as the semiconductor photocatalyst functions as a pool of electrons and holes, it can be exploited in multi-electron transfer processes (e.g., for H_2 and O_2 evolution from water). Here, the presence of a redox catalyst (such as Pt or RuO_2) on the surface can improve

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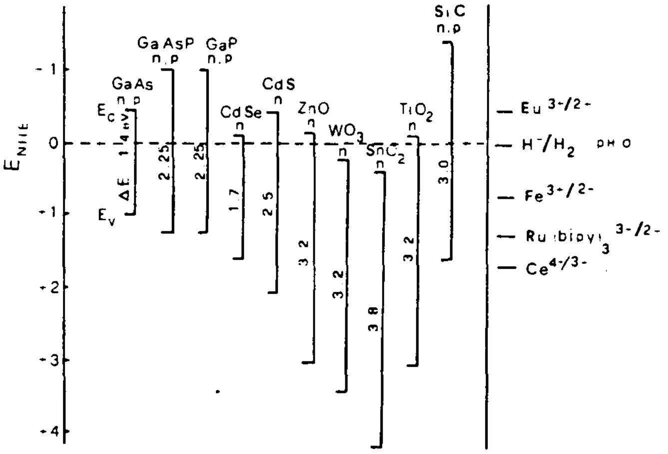


Figure 1 – Position of the valence and conduction band edges at the surface of various semiconductors in contact with an aqueous electrolyte at pH 1.

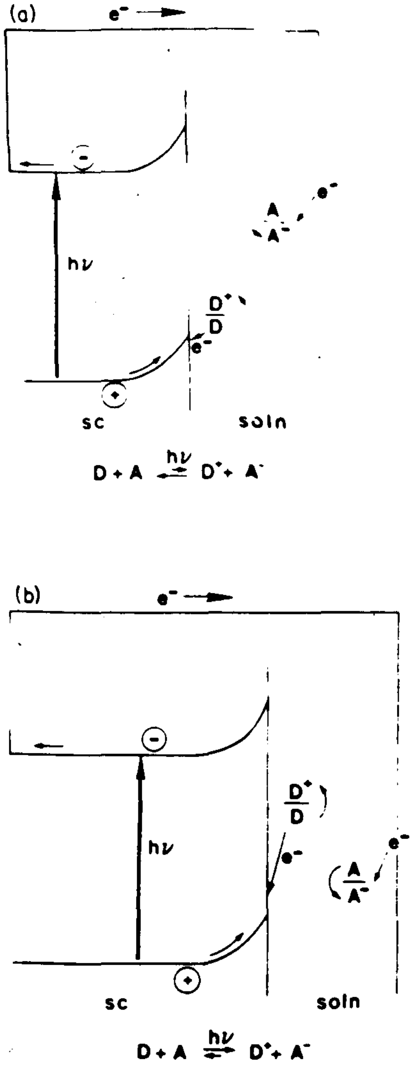


Figure 2 – Schematic presentation of photosynthetic (a) and photocatalytic (b) systems.

the catalytic efficiency of the particle.[2,16] In this regard, semiconductor particulate systems present several advantages among which are high extinction coefficients and fast carrier diffusion to the solid/water interface. These properties lead to large catalytic surfaces and higher efficiencies; also, there are fewer constraints on the type of material (polycrystalline) and on the physical state of the reactants (gas, liquid, or solid phases). Finally, the particulate systems are simpler and less expensive to assemble and to use. Consequently, light-driven redox reactions with semiconductor powders have found wide application in photocatalytic ($\Delta G < 0$) as well as in photosynthetic processes ($\Delta G > 0$). These two processes are depicted in Figure 2.

3. WATER CLEAVAGE – PHOTOGENERATION OF OXYGEN

The generation of oxygen from the light-induced photocleavage of water is a topic of much current focus.[2] The oxygen formation reaction is very important in the design of photochemical devices that attempt to achieve water photolysis. The production of a molecule of oxygen from water via the photoredox decomposition is, mechanistically, a difficult process that involves a concerted four-electron transfer event (reaction 1). One successful approach to

$$2H_2O \longrightarrow O_2 + 4H^+ + 4e^- \qquad [1]$$

resolving this difficulty implicates the utilization of semiconductor particulate matter as the light harvesting units. These have been, and continue to be investigated extensively by several researchers throughout the world. Much of the attention in these investigations is directed at TiO_2 (anatase) used not only as a semiconductor (the light harvester) but also as a support for appropriate redox catalysts (e.g., Pt, RuO_2, etc...). While TiO_2 particles loaded with noble metal catalysts and/or metal oxides efficiently produce hydrogen under illumination from the photosplitting of water, the simultaneous liberation of stoichiometric amounts of oxygen is not always observed.[17-21] For example, irradiation of Rh- or Pt-loaded TiO_2 aqueous dispersions (argon-purged, ambient temperature, closed vessel) affords detection only of hydrogen in the gaseous phase.[22, 23] The cyclic fashion in which these systems operate suggests the additional involvement of the TiO_2 particles as oxygen carriers. That is, the oxygen formed from the photocleavage of water is photo-uptaken by TiO_2 producing, initially, the superoxide ion O_2^- and subsequently the peroxide ion O_2^{2-} that binds to the surface of the titanium oxide.[22] Recently, Duonghong and Gratzel[24] have outlined a procedure for the specific and quantitative analysis of such peroxo species on the TiO_2 particle surface.

Ineeed, Munuera and co-workers[25] have shown that O_2 is readily photo-adsorbed on TiO_2 under bandgap irradiation leading to the formation of different oxygenated species (O^-, O^{2-}, O_2^-, O_3^-, O_3^{3-}); these have been identified by electron paramagnetic resonance and infrared techniques.[26] Munuera[27] further reports that H_2 evolution occurs upon irradiation of a rhodium-doped TiO_2 sample in 1 *M* NaOH, but O_2 was never detected. By contrast, neither hydrogen nor oxygen were observed on irradiating naked TiO_2 suspensions under the same experimental conditions. In an analogous experiment, injection of oxygen into a flask (same photo-reactor and same light intensity as previously used) containing TiO_2/Rh or naked TiO_2, followed by irradiation at bandgap energies lead to an immediate photo-uptake of oxygen; evolution of hydrogen from a sample of TiO_2/Rh was almost hindered. The rate of O_2 photo-uptake was rather similar for both naked TiO_2 and for TiO_2/Rh. This suggests[27] that the process of O_2 photo-uptake takes place mainly on the oxide surface. It appears, on the basis of the presently available data from the work of Munuera[27] and Gratzel,[22] that the yield of O_2 in the gaseous phase depends on three factors: (i) the rate of oxygen photo-uptake, (ii) the rate of formation of peroxide, and (iii) the rate of the thermal decomposition of the peroxide formed. In fact, as previously pointed out by Grätzel,[22, 28] flushing the aqueous semiconductor dispersion with argon, during or after a short period of irradiation, restores the activity of the semiconductor suspension. Apparently, this flushing procedure prevents the formation of the peroxide by removing the oxygen as soon as it is formed. It is worth noting that the nature of the surface of the oxide (recalling that TiO_2 is the most studied system) plays an important role in the oxygen photo-uptake process.[29] The quantity of O_2 photo-uptaken is much greater on a highly hydroxylated TiO_2 surface than on a poorly hydroxylated surface.[29]

The above considerations suggest that OH groups on the TiO_2 surface are important elements in the photo-uptake event; they confirm previous results.[25, 27] For example, in the recombination of H_2 and O_2 on differently prepared TiO_2 suspensions, the amount of oxygen that disappears under irradiation is greater than that expected from the stoichiometry of the H_2/O_2 recombination reaction, and is very much dependent upon the extent of hydroxylation of the TiO_2 surface.[29] This observation is rationalized in terms of the formation of peroxo species bound to the surface. The difference is even more remarkable when the TiO_2 surface is highly hydroxylated. Moreover, The H_2/O_2 recombination reaction on TiO_2/Rh particles follows the expected stoichiometric ratio of 2:1 if the reaction occurs in the dark.[27] By contrast, under irradiation, oxygen photo-uptake immediately occurs while hydrogen is photo-generated at increasing rates as the quantity of O_2 becomes exhausted in the gaseous phase.

In order to elucidate the relation between the nature of the surface of TiO_2 and the photo-generation of oxygen in the water splitting reaction, the recent work of Oosawa and Grätzel[30] is worth considering. In experiments designed to study the effect of surface OH groups in the reaction between valence band holes (h^+_{vb}) and water to produce O_2, these authors noted a remarkable enhancement in oxygen formation with removal of such OH groups from the TiO_2 surface. The degree of hydroxylation was adjusted by thermal treatment and analyzed by titration techniques.[31] In these studies,[30] the reaction between photo-generated h^+_{vb} (TiO_2) and water was monitored using Ag^+ as an electron trap to suppress h^+_{vb}/e^-_{cb} recombination. The conduction band electrons, e^-_{cb}, produced by bandgap irradiation of TiO_2, reduce Ag^+ to Ag^o, while h^+_{vb} are free to react with water to envolve oxygen, following the net reaction 2. The molar ratio, *r*, between Ag^+ and O_2 must be 4.

$$4Ag^+ + 2H_2O \xrightarrow[TiO_2]{hv} 4Ag + 4H^+ + O_2 \qquad [2]$$

$r = 4$ was observed for TiO_2 powders possessing a low OH density resulting from thermal treatment at high temperature, while values of $r > 4$ were obtained with hydroxylated powders, thus confirming earlier results.[29] This supports the suggestion by Grätzel[22] that the valence band hole reaction with water on highly hydroxylated TiO_2 does not lead directly to oxygen, but rather to an intermediate, presumably a peroxo-titanium complex[22, 23] whose decomposition is slow (probably a μ-peroxo type complex which dissolves in 1 *M* NaOH but remains on the TiO_2 particle surface under neutral pH conditions). ZnO aqueous dispersions have also been studied.[32] In this case, H_2O_2 is formed as the product of the oxidation of water.

In addition to Ag^+ ion, other species have been employed as electron acceptors in the bandgap irradiation of TiO_2.[29,33] It is noteworthy that O_2 envolves when $BrO_3{}^-$ ions are used as electron traps in the presence of TiO_2/RuO_2 suspensions;[33] $BrO_3{}^-$ is a very important intermediate in several cycles for the termochemical splitting of water.[34]

Reports have recently appeared on the visible light-induced oxygen formation in aqueous dispersions of semiconductors.[35-38] WO_3 and CdS suspensions have been utilized extensively for this purpose. Krasnowsky[39] was the first to observe formation of oxygen by visible light irradiation of WO_3 aqueous dispersions (reaction 3).

$$4h^+_{vb}(WO_3) + 2H_2O \longrightarrow O_2 + 4H^+ \qquad [3]$$

Ferric ions were the conduction band electron traps, giving the overall photo-reaction 4.

$$2H_2O + 4Fe^{3+} \xrightarrow[WO_3]{hv} 4Fe^{2+} + O_2 + 4H^+ \qquad [4]$$

Darwent and Mills[40] recently carried out a more detailed investigation of this photoreaction 4; the Fe^{2+} ions formed compete with water for the h^+_{vb} (WO_3). Employing silver ion, instead of ferric ion, as the electron acceptor leads to an improvement in the O_2 yield.[35] Figure 3 compares the behaviour of the two electron acceptors, Ag^+ and Fe^{3+}, in a long-term experiment for which a Suntest lamp was the light source simulating AMI solar radiation (the global irradiance of this lamp was 70 mW/cm^2). An improvement in the rate of oxygen formation is obtained if the redox catalyst RuO_2 is deposited on the surface of WO_3, and Fe^{3+} ions are the electron acceptors. Analogous results have been obtained earlier with TiO_2[29] and confirm the activity of RuO_2 as an excellent redox catalyst for oxygen

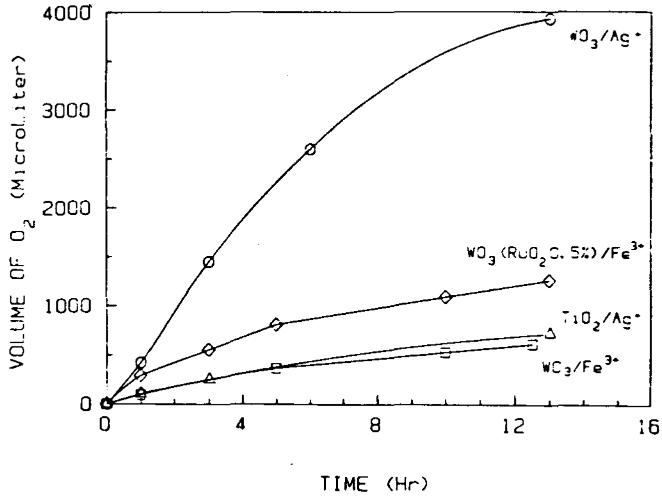


Figure 3 – Oxygen generation from irradiated aqueous solutions of 5 x 10^{-2} M $AgNo_3$ and 10^{-2} M $FeCl_3$ in the presence of WO_3, WO_3/0.5 wt.% RuO_2, or TiO_2. The catalyst concentration was 8 g/L, initial pH 4, irradiation was with a Suntest lamp.

evolution.[40 - 42] Oxygen bubbles are readily visible on the WO_3 particles under the simulated sunlight irraddiation utilizing Ag^+ rather than Fe^{3+} to trap the e^-_{cb} (WO_3). The activity of TiO_2 and WO_3 dispersions for O_2 evolution in the presence of Ag^+ is compared in Figure 3. The initial rate in TiO_2/Ag^+ suspensions is approximately 5 times lower than the rate for WO_3/Ag^+ suspensions, for the same amount of powder (8 g/L) and the same Ag^+ concentration (5 x $10^{-2}M$). The molar ration of O_2 produced to Ag^+ consumed in the reaction was always 1:4 when WO_3 was employed as the semiconductor. This was not the case for untreated TiO_2, as pointed out earlier.[29, 30] One of the advantages of WO_3 suspensions over TiO_2 or ZnO is the smaller bandgap of WO_3 (2.5 ev vs. $\geqslant$ 3 e V) corresponding to a fundamental absorption edge of 496 nm. Oxygen generation from water can therefore be driven by visible light, particularly important for solar energy applications.

CdS dispersions are attractive alternatives for the visible light-induced photosplitting of water,[43-45] owing to the appropriate position of the conduction band and valence band redox levels; these redox equivalents cause the reduction and oxidation of water. When CdS particles are irradiated in the presence of water, H_2 is generated at the conduction band; the valence band holes lead to photocorrosion of CdS to S (oxidation of S^{2-} of CdS) with the concomitant release of Cd^{2+} ions into the bulk of the aqueous solution. Our previous investigagions[43-45] have pointed out hat loading RuO_2 onto CdS particles surface leads to an enhancement of the stability of the semiconductor towards the photo-corrosion process. This was recently demonstrated by showing that CdS/RuO_2 is virtually capable of evolving O_2 in the presence of a suitable e^-_{cb} acceptor.[37]

Another interesting semiconductor which is presently under active investigation for O_2 evolution from water is In_2O_3.[36] In_2O_3 has a bandgap of ~2.5 eV, comparable to that of WO_3 particles.[46, 47] Erbs and co-workers[37] have compared the activity of In_2O_3 suspensions with WO_3 suspensions in the presence of Ag^+ as the electron acceptor. It appears that In_2O_3 is $\approx$10 times less efficient than WO_3 in mediating water ocidation. A very low efficiency was also reported by McCann and Brockis[48] and by Lioh and co-workers[49] who attributed the low efficiency to the fact that the visible and near-uv light absorption of In_2O_3 corresponds to an indirect transition, rendering the absorption length much greater than the diffusion length of the valence band holes.

Great efforts are presently being expended in finding new semiconductors and new devices to improve the efficiency of the photo-oxidation of water in a water splitting photochemical cycle. The goal is to achieve yields that might prove competitive with other already existing cycles (electrochemical, photo-electrochemical, and thermal).

4. HYDROGEN SULFIDE CLEAVAGE

The wide range of interest of sulfur compounds in industrial processes has rendered the chemistry of sulfur a field of intense research. For example, H_2S is one of the major constituent of natural gas,[50] is the product of the hydrodesulfurization of petroleum and is the final product in the removal of sulfur from coal. High percentages of hydrogen sulfide are also contained in sour gas and in steam from geothermal sources. Much of the research is dedicated to the removal of sulfur from petroleum, coal, and natural gas, as well as from other energy sources where sulfur is found. This is necessitated to avoid oxidation of sulfur during the combustion process that could lead to a large increase of sulfur oxides (SO_2, SO_3, etc...) in the atmosphere and thereby generate severe environmental problems (acid rain, corrosion, smog,...).[51]

The H_2S produced in the industrial processes noted above is presently treated by the Claus process, whereby H_2S is burned in an atmosphere os oxygen to form water and sulfur. Every year, over 10 million tonnes of H_2S are produced and this amount is expected to increase in the future. If hydrogen were recovered from H_2S, nearly 8 x $10^9 m^3$ per year of H_2 could be produced.[52] Achievement of this goal is not only desirable, but is exciting and is being pursued actively in different laboratories.

Several thermochemical cycles that utilize metal sulfides as catalysts have been proposed to avoid the drastic conditions required to get H_2 from H_2S by direct thermal decomposition (T > 1800°C).[52] The main problem in using metal sulfides is the sintering of the catalyst at the high temperatures of the process.[53-55]

The photochemical cleavage of hydrogen sulfide was reported for the first time on RuO_2-loaded CdS particles.[34, 56] The mechanism of this cleavage involves the oxidation of S^{2-} ions (or HS^-) by the valence band holes of CdS, h^+_{vb}(CdS), produced by bandgap irradiation of CdS (bandgap = 2.4 eV, threshold wavelenght = 520 nm), with the concomitant reduction of protons to hydrogen by the conduction band electrons, e^-_{cb}(CdS). Several other catalysts have been studied and different devices are presently under active investigation. Reber[57] for example loaded CdS with Pt and obtained a quantum efficiency of 0.34 for the protocleavage of H_2S in the presence of $H_2PO_2{}^-$ ions. A quantum efficiency of 0.12 was recently reported by Mackor and co-workers,[58] using RuS_2-loaded (0.5 wt.%) CdS in an alkaline solution of H_2S and $So_3{}^{2-}$ ions. Micic[59] also obtained an efficiency of 0.12 using RhO_x-loaded CdS in Na_2S solution.

In our laboratories, we have been successful in preparing a catalyst (from $RhCl_3$ and CdS) with which H_2 evolution occurs with a quantum efficiency of 0.45 ± 0.05 and an overall energy conversion efficiency close to 3% for alkaline solutions of Na_2S in the presence of SO_3^{2-} ions.[60] A transparent colloidal CdS sol loaded with RuO_2 has also been employed instead of the powder,[61] and a rhodium-loaded CdS sol in a surfactant vesicle has been tested.[62] In the latter case, rhodium was photo-deposited onto CdS particles prepared in the dihexadecylphosphate surfactant vesicle.

Very attractive is the approach of the semiconductor supported on polymers. Meissner et al.,[63] have used membranes consisting of CdS particles (~40 μm diameter) physically embedded in a polyurethane film and have studied a number of photolytic processes. Kuczynski and co-workers[64] prepared dispersed CdS in Nafion(125) membrane and have examined its photochemical and photophysical properties. Recently, anoter study on CdS-Nafion(117) was reported[65-67] for H_2S splitting. The build-up of polysulfides, S_n^{2-}, when H_2S is oxidized in the presence of colloidal CdS was prevented by heating the CdS (Nafion) system at 300°C in O_2 leading to the formation of SO_4^{2-}.

Another interesting finding under investigation in our laboratories is the combination of two semiconductors (CdS and TiO_2) to improve charge separation on irradiated CdS particles.[68, 69] Figure 4 shows the H_2 evolution rate for the visible light irradiation of two CdS dispersions in 0.1 M Na_2S, 1 M NaOH, and 50 mg of powder. In one case, the RuO_2 was directly loaded onto CdS particles; in the other case, TiO_2 particles were loaded with the same amount of RuO_2 and naked CdS was excited by light.[68] The mechanism of effective charge separation involves inter-particle electron transfer from CdS to TiO_2; this is responsible for the improvement in the H_2 evolution rate and for the suppression of charge recombination in the excited semiconductor which always decreases the efficiency of the system (e^-_{cb} + h^+_{vb} recombination; reduced species + h^+_{vb}; oxidized species + e^-_{cb}). In this inter-particle electron transfer process, reduction occurs on the TiO_2/RuO_2 particles while oxidation occurs on naked CdS.

The mode of preparation of the catalyst plays an important role in the photochemical cleavage of H_2S.[69,70] The preparation of the poweder (CdS or TiO_2), the etching, and the presence of ions are determinant in the reproducibility of the process. Figure 5 compares the H_2 evolution rates for the same experimental conditions but with different CdS and TiO_2 preparations.[69] Two different CdS preparations were employed (CdS-F(2) and CdS-M9) and two different TiO_2 preparations were tested (TiO_2-B and TiO_2-M4bis) loaded with 0.2 wt.% RuO_2 and 0.5 wt. % RuO_2. It is also clear (cf. Figure 5) that for the same TiO_2/RuO_2 sample, the use of different CdS preparations can alter the reaction rate. As well, keeping constant the CdS but changing the TiO_2/RuO_2 we observe the same effect.[69] This suggests that the photocatalytic activity is related to the electronic structure of the solid and to the surface modification. The best combination of CdS and TiO_2/

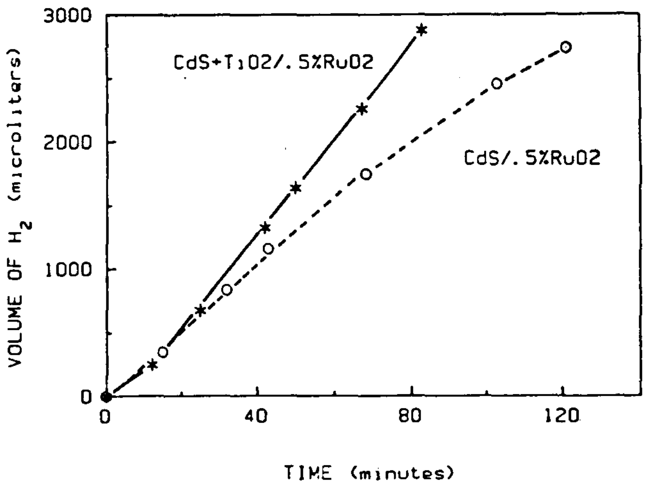


Figure 4 – Volume of hydrogen (STP) produced by visible light irradiation of tow CdS dispersions. In one case the RuO_2 is directly loaded (wt.%) onto CdS particles (dashed line); in the other case, TiO_2 particles are loaded with the same amount of RuO_2 and naked CdS is excited by light (solid curve).

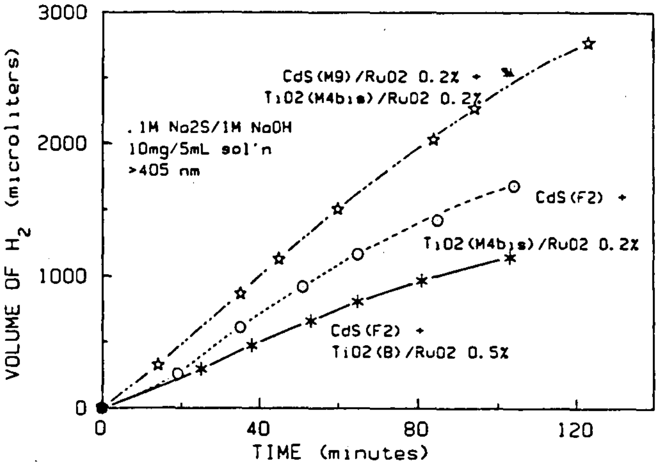


Figure 5 – Volume of hydrogen (STP) generated by visible light irradiation of three CdS dispersions containing 0.1 M Na_2S and 1 M NaOH. The semiconductor excited by light is CdS.

RuO_2 for the photocleavage of H_2S in alkaline solutions (1 M NaOH) is obtained using the semiconductor dispersions prepared by Visca of Montedison (Italy), namely, CdS-M9 and TiO_2-M4bis.[69]

4.1. Effect of Anions and Surfactants

Anions play and important role in the photochemical cleavage of hydrogen sulfide. They increase the rate of H_2 production. In the oxidation of S^{2-} so formed can efficiently compete with protons for the reduction sites (e^-_{cb}) and can act as optical filters preventing absorption of light by the CdS dispersion. Any anion that can react with polysulfides or that can prevent their formation could prove, at least in principle, to be a good candidate for this process. As an example, Figure 6 illustrates the effect of adding SO_3^{2-} ions (0.1 M) to a solution of 0.1 M Na_2S and 1 M NaOH on the H_2 evolution rate in the presence of CdS/RuO_2 (1 wt.%) particles.[71,72] It is evident that addition of SO_3^{2-} ions results in an improvement in the hydrogen evolution rate, a result of the formation of $S_2O_3^{2-}$ ions (reaction 5):

$$S_n^{2-} + SO_3^{2-} \longrightarrow S_2O_3^{2-} + S_{n-1}^{2-} \qquad [5]$$

Reaction 5 is particularly atractive for various reasons. First, SO_2 is a pollutant (just like H_2S) which forms in the combustion of sulfur compounds. It can be trapped in alkaline solution as SO_3^{2-}. In this approach, the transformation of SO_3^{2-} to $S_2O_3^{2-}$ at the expense of S^{2-} is a very interesting process from and environmental point of view. In addition, $S_2O_3^{2-}$ is a useful product, widely used in industrial processes such as photography. Another advantage is that the rate of hydrogen production is favourably affected, making possible the sustainement of the photocleavage reaction for longer periods.

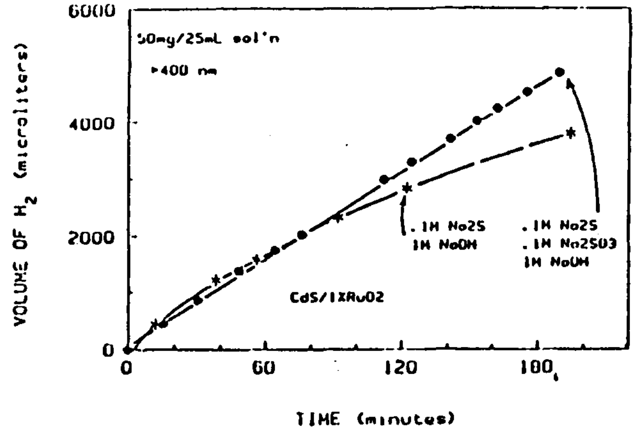


Figure 6 – Volume of H_2 (STP) produced by visible light irradiation of RuO_2 loaded (1 wt.%) CdS in the presence and absence of sulfite ions in solutions 0.1 M in Na_2S and 1 M in NaOH.

One interesting anion that was employed to scavenge S_n^{2-} ions is the hypophosphite ion $H_2PO_2^-$.[57] The reaction is very much similar to the one in the presence of sulfite ions except for the fact that all of the polysulfide anions are recycled (reaction 6). Also, in

$$S_2^{2-} + H_2PO_2^- + 3OH^- \longrightarrow 2S^{2-} + HPO_3^{2-} + 2H_2O \quad [6]$$

this case, S_n^{2-} ion accumulation is suppressed.

A very promising approach in the hydrogen sulfide cleavage reaction is the use of surfactant-coated CdS as a catalyst. We have shown earlier[71] that using a sodium dodecylsulfate solution (below the CMC) in the presence of CdS, H_2 evolution occurs at a yield comparable to that observed for RuO_2-loaded CdS. This indicates a positive contribution of the surfactant, probably due to the change in the local pH around the CdS particle. It was surprising to observe that the use of a cationic surfactant (CTAB, for example) does not alter the reaction rate.[71] One possible reason for this is the positive charge created around the particle because of the adsorption of the surfactant on the CdS particle surface. The possibility of employing surfactants instead of RuO_2 as 'catalysts' for the reaction opens up the possibility of running this system at lower costs and in a more facile way. Surfactants are usually inexpensive and easy to prepare, compared to precious metals and metal oxides. Moreover, they adsorb well on CdS particles below the CMC of the surfactant; above their CMC, surfactants preferentially form micelles instead of being adsorbed on the semiconductor particles.

4.2. The Thiosulfate Cycle

One of the more significant findings in our laboratories is the reduction of $S_2O_3^{2-}$ ions to S^{2-} and SO_3^{2-} on TiO_2, in alkaline solution and under illumination by uv light.[73] Under these experimental conditions, the consumption of thiosulfate leads to the appearance of S^{2-} and SO_3^{2-} ions in a 1:2 stoichiometric ratio. During irradiation and in the absence of O_2, neither SO_4^{2-} not $S_2O_6^{2-}$ ions formed.[73] The proposed mechanism involves:

(a) reduction of thiosulfate ions by $e^-_{cb}(TiO_2)$,

$$S_2O_3^{2-} + 2e^-_{cb}(TiO_2) \longrightarrow S^{2-} + SO_3^{2-} \qquad [7]$$

(b) oxidation of $S_2O_3^{2-}$ to $S_4O_6^{2-}$ by $h^+_{vb}(TiO_2)$,

$$2S_2O_3^{2-} + 2h^+_{vb}(TiO_2) \longrightarrow S_4O_6^{2-} \qquad [8]$$

(c) disproportionation of $S_4O_6^{2-}$ in alkaline solution according to reaction 9:

$$1.5H_2O + S_4O_6^{2-} \longrightarrow SO_3^{2-} + 1.5S_2O_3^{2-} + 3H^+ \quad [9]$$

The net overall photoreaction is

$$1.5H_2O + 1.5S_2O_3^{2-} \xrightarrow{hv} 2SO_3^{2-} + S^{2-} + 3H^+ \quad [10]$$

which is an energy storing reaction (0.38 eV, pH 14, 298K).

Following the above results, we looked at the possibility of combining this reaction 10 to the photogeneration of hydrogen from hydrogen sulfide solutions.[73] Figure 7 describes the essential features of a two-compartment system, where hydrogen is produced in the CdS/RuO_2 containing half-cell and S^{2-} is concomitantly oxidized to $S_2O_3^{2-}$. The thiosulfate is then transferred to a second half-cell containing TiO_2 particles, where dismutation of $S_2O_3^{2-}$ is light-driven. One advantage of this cycle is that 3 moles of H_2 are produced (reaction 11). By contrast, in the simple H_2S photocleavage process, only one mole of hydrogen is produced. Reaction 11 stores a significant quantity of

$$3H_2O + S^{2-} \xrightarrow{hv} SO_3^{2-} + 3H_2 \qquad [11]$$

light energy (ΔG^o_{298} = +3.2 kcal/mol). An additional advantage of this cycle is that there is no accumulation of either sulfur or thiosulfate, thus making the photoreaction very efficient and clean.

4.3. Concluding Remarks

Several suggestions have already been put forth on the feasibility of a large scale plant for the photosplitting of H_2S.[50,74] The reaction is efficient and the recovery of H_2 from waste materials (H_2S and SO_2) is a very attractive goal. Many problems still remain, however, such as catalyst stability and product separation in a large scale. These problems notwithstanding, the coupling of sunlight to an artificial source of energy affords a very atractive process from and economical point of view, particularly in areas of low land value and at near-equatorial latitudes. Added to the H_2 recovery, a valuable and clean fuel, the process(es) cited herein can be used in the clean-up of sulfide contaminated waters and wastes. As we have noted in this paper, the addition of SO_3^{2-} or $H_2PO_2^-$ ions a positive asset to the process, meaning that other contaminants can be removed from the environment and used again to produce energy.

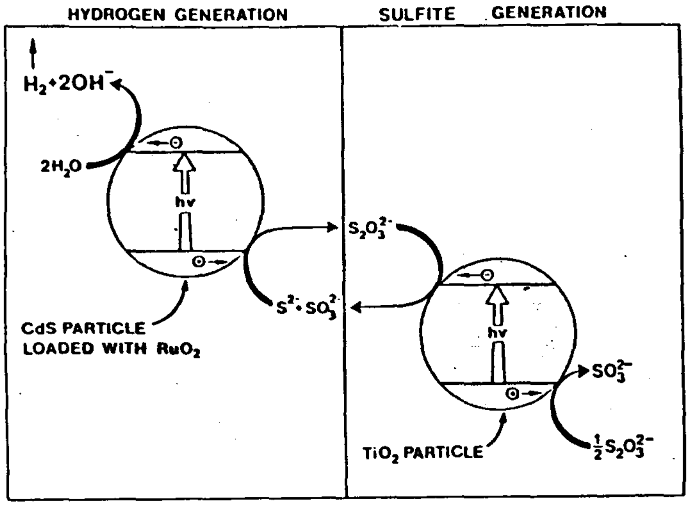


Figure 7 — Diagram showing the coupling of two processes in a cyclic photosystem for hydrogen and sulfite generation.

Work is now being directed towards the environmental impact of the H_2S/SO_3^{2-} process, much of which going to improve the efficiency and the stability of the catalyst for long periods.

5. PHOTOCATALYTIC RECATIONS OF ORGANIC COMPOUNDS

5.1. Photoassisted Water-Gas Shift Reaction

When water acts as the electron acceptor and carbon monoxide CO as the hole scavenger, the process corresponds to the photoassisted water-gas shift reaction (WHSR). Reaction 12 is thermodynamically

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad [12]$$

a down-hill process with a small ΔG^o value.

The activity of platinized TiO_2 has been investigated in the temperature range 0-60°C and shows that the reaction is zero order both in [CO] and [water] and first order in light intensity.[75] The quantum efficiency was found to be 0.5% and the photoassisted decomposition of water molecules proved to be an important part of the WGSR. mechanism.

The effect of catalyst preparation has been investigated in detail;[76] the influence of Pt loading beyond 2% is minor indicating that the rate is not controlled by the amount of Pt above this deposit. Also, the presence or absence of strong metal support interactions or the different method of depositing (photodecomposition or impregnation) Pt have no influence on the process. The increase in the rate upon reducing (hydrogen doping) TiO_2 was attributed primarily to the increased rate at which holes move to the surface, resulting from the removal of lattice oxygen atoms leaving defects and Ti^{3+} ions which make TiO_2 more n-type and increase the conductivity of the powder.

Another factor that increases the rate of photoassisted WGSR is NaOH loading; an improvement of 16 times is observed for a 3.5 wt.% NaOH catalyst,[76] suggesting that the process in which hydroxide ion donates its electron to the surface hole is rate determining. Thus, the parameters which increase the surface hole population, such as reduction with hydrogen, light intensity and NaOH loading, improve the performance of the process. A recent investigation on the kinetics of the reaction gives similar results.[77] Based on platinum coverage studies, it was proposed that the periphery of deposited Pt islands is involved in the photogeneration of hydrogen.

Other semiconductor particles, namely silicon carbide (SiC) and cadmium sulfide (CdS), were investigated and WGSR was also found to be affected.[78] Since the hydrogen evolution in WGSR increases through daylight lamp illumination of SiC (bandgap 3.0 e V), it was inferred that there are energy levels between the valence and conduction bands, probably arising from surface states. In the case of the low bandgap material, CdS, a mechanism similar to that reported above for TiO_2 has been proposed. Application of Rh deposit onto the surface of both SiC and CdS drastically enhances the amounts of H_2 produced by a factor of ~ 20-70. By contrast, RuO_2 exhibits a slight depressing effect on hydrogen evolution.

5.2. Photoinduced Hydrogen Evolution from Fossil Fuels and Water

The direct reaction of carbon with water using thermal energy is known as the water gas reaction and takes place around 1000°C. The use of this reaction under photocatalytic conditions at low temperatures (room temperature or 60°C; reaction 13, $\Delta G^o = 7.5$ kcal/mol)

$$H_2O_{(g)} + 1/2\, C_{(s)} \longrightarrow H_2 + 1/2\, CO \qquad [13]$$

is interesting in the light of current interest on the gasification of large coal reserves.

The products obtained from active carbon over illuminated TiO_2/Pt are H_2, CO_2, and a small amount of O_2.[79] On the basis of the experimental results, a mechanism was proposed involving the reaction of the surface carbon atoms with oxygen species giving a layer of various oxides of carbon. Subsequently, these surface species are decomposed and further oxidized to CO_2. The kinetics are similar to those of WGSR showing an almost zero-order dependence of the rate on H_2O pressure; activation energies are also similar. The decline of the H_2 formation in a given run is presumably due to the accumulation of H_2 competing with carbon for the oxygen species. The long term decrease arises however from the loss of a good contact between the catalyst and carbon, since the initial rate can be reproduced by remixing the sample.

Similar results were obtained whan a mixture of active carbon and TiO_2/RuO_2 is illuminated in the presence of gas-phase H_2O.[80] Traces of CO were also formed and in addition CO and H_2 were the major products when H_2O is in the liquid phase. These differences arise from the different oxidizing capability of TiO_2/Pt compared to the TiO_2/RuO_2 system. Various fossil fuels such as coal, tarsands, and pitch have also been found to react with water, producing both hydrogen and CO_2 from an early stage of irradiation. The photo-catalytic oxidation of the model compounds, especially linear hydrocarbons and benzene was also investigated.[81]

5.3. Photoinduced Hydrogen Generation from Alcohols

Photocatalytic hydrogen evolution from alcohols has been investigated in the presence of various semiconductor particles. Hydrogen is evolved in sustained amounts when pure-primary and seconary alcohols (and ethylene glicol) are irradiated with UV light in the presence of TiO_2/Pt[82-85] (see Table 1; the catalyst is TiO_2 P25 Degussa).

Various unsaturated alcohols (eg. allyl and cinnamyl alcohols, citronellol and geraniol) can be dehydrogenated under similar conditions.[86] Other compounds containing a hydroxy group and an α-hydrogen (lactic and tartaric acid, triethanolamine) also produce H_2.[86] The main product of the reaction (together with hydrogen) was shown to be the corresponding aldehyde (or ketone) for the saturated alcohols and for citronellol. For alcohols with a conjugated double bond, the corresponding saturated alcohol can also be formed. Only traces of alkanes, alkenes, and CO_2 were detected.

Table 1

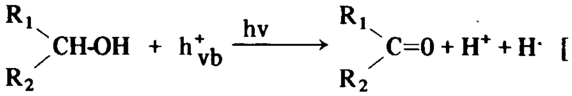
Hydrogen evolution rate in ml/h from pure methanol in the presence of TiO_2 catalyst, 1 g/l, Pt 2 wt.%, UV light, 450 W Xe lamp, Ar saturated solution, volume 25 ml

Alcohol	$r(H_2)$ ml/h
Methanol	14
ethyleneglycol	10.5
ethanol	9
n-propanol	8
iso-propanol	7
n-butanol	5
iso-butanol	3
t-butanol	0.1

The data were averaged over the first hour of irradiation.

The influence of water content (a plateau is reached when ~ 10% of methanol or ethanol is present) suggests that one of the steps of the reaction involves and adsorbed species.

After the electron/hole pair formation at the surface of the semiconductor, the process goes through



$$\begin{matrix}R_1\\ R_2\end{matrix}\!\!>CH\text{-}OH + h^+_{vb} \xrightarrow{hv} \begin{matrix}R_1\\ R_2\end{matrix}\!\!>C{=}0 + H^+ + H^\cdot \qquad [14]$$

followed by

$$H^+ + H^\cdot + e^-_{cb} \xrightarrow{Pt} H_2 \qquad [15]$$

The process corresponds to alcohol dehydrogenation (an endoergic process, ΔG^o = 10-15 kcal/mol) and the order of the H_2 evolution rate of Table 1 probably reflects the tendency of adsorption and perhaps of pre-dissociation of the alcohols at the catalyst surface.

Noteworthy are the effects of differently prepared TiO_2 catalysts[84] and the effect of different metal or metal oxide loading, Pt being the most effective;[84-88] no beneficial effect is however shown by RuO_2 loading[84,85] (see Figure 8).

A detailed investigation of the influence of Pt[83] showed that deposition through impregnation and subsequent H_2 reduction lead to homodispersed particles of mean diameter

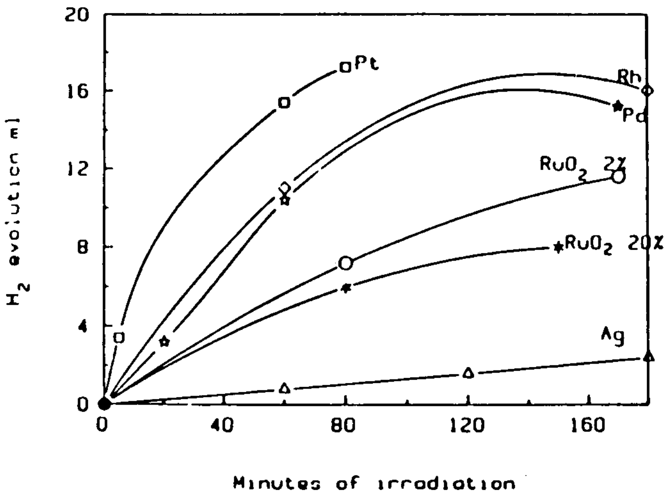


Figure 8 – Hydrogen evolution for methanol oxidation in the presence of TiO_2 loaded with different metals and RuO_2; UV light, argon saturated, 25 ml solution.

~ 2 nm and that an optimum initial rate of H_2 evolution was obtained in the 0.1-1 wt.% range. This maximum is tentatively attributed to an optimum attraction of the free electrons of TiO_2 by Pt crystallites, which corresponds to an optimum ratio of the acidic and basic sites involved in the abstraction of hydrogen atoms from the alcohols on TiO_2.

Inasmuch as no H_2 evolution was observed when a cut-off filter (eliminating photons of wavelength shorter than the TiO_2 absorption edge) is interposed, in order to allow the system to work under visible light, experiments were carried out with dye sensitized TiO_2.[84] Another possibility is the use of low bandgap semiconductors, such as CdS, WO_3,[84,99,90] and Si.[91] The use of other photocatalysts based on Mo(VI)/Al_2O_3 and MO(VI)/Pt/Al_2O_3 has been exploited recently.[92] For methanol, the main products are CH_4 and H_2, although CO_2 and C_2H_6 are also produced in trace amounts. In this case, the tetrahedral monomeric oxomolybdenum species are the photoactive sites. In the case of n-propanol, production of H_2, CH_4, C_2H_6, propanol, ethanol, and formaldehyde are observed.[92]

A considerable improvement toward high efficiency under visible light irradiation has been recently obtained through the combination of semiconductor (CdS and TiO_2) dispersions loaded with suitable redox catalysts. The coupling of CdS with TiO_2/Pt (anatase) powders yields catalytic suspensions more efficient than CdS/Pt dispersions (see Figure 9).[93] It was suggested that the former system takes advantage of an inter-particle electron transfer mecnnism which leads to vectorial physical displacement of the charge carriers on semiconductor particles.[68] The hydrogen evolution rate is 2.27, 3.29, and 2.83 ml/h for methanol, ethanol, and i-propanol (under the conditions of Figure 9, but Pt is loaded at 10 wt.%). The overall energy conversion efficiency is 2% at $\lambda > 405$ nm.

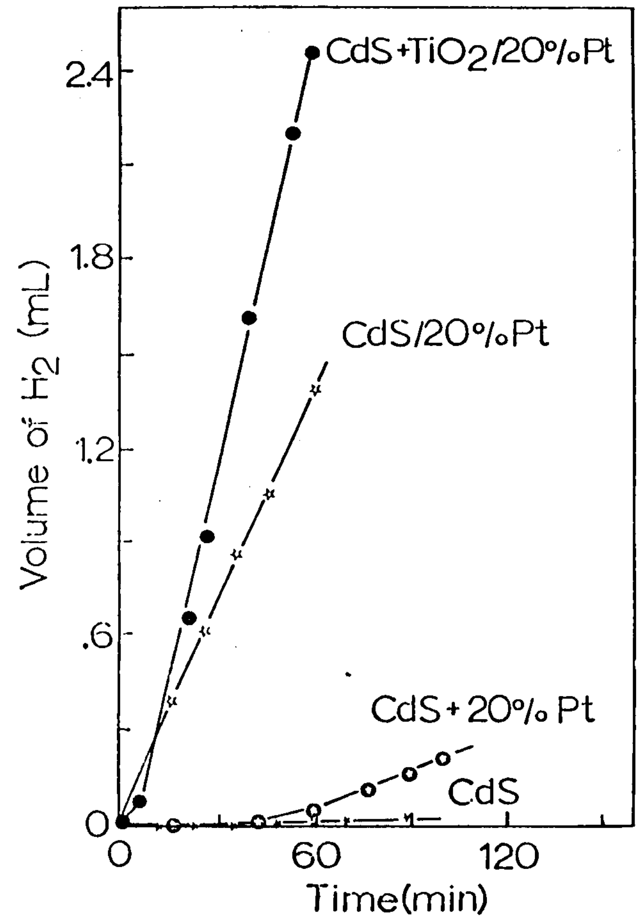


Figure 9 – Volume of hydrogen (STP) produced as a function of irradiation time in the dehydrogeneration of pure methanol in the presence of various catalytic dispersions; 10 mg of catalyst per 5 ml solution; Pt 20 wt.%; visible light irradiation ($\lambda > 405$ nm); 1000-Watt Hg/Xe lamp; argon saturated solution.

5.4. Photocatalyzed Decarboxylation of Organic Carboxylic Acids

The heterogeneous photocatalytic decomposition of aliphatic carboxylic acids on TiO_2 powder yields the corresponding alkane according to the reaction 16. Notable amounts of H_2 and of other

$$R\text{-}COOH \xrightarrow[TiO_2/Pt]{h\nu} R\text{-}H + CO_2 \qquad [16]$$

alkanes (R-R) are produced.[94] The reaction is not specific for TiO_2 but illumination of WO_3 gives similar results.

Detailed investigations have been carried out on the reaction involving acetic acid/acetate mixtures in the presence of TiO_2/Pt.[95] Anodic oxidation of acetate produces the methyl radical according to

$$CH_3COO^- + h^+_{vb} \longrightarrow CH_3{}^{\cdot} + CO_2 \qquad [17]$$

The cathodic process is the formation of adosrbed hydrogen on Pt sites (reaction 18). Methane can be produced (equation 19) or ethane

$$H^+ + e^-_{cb} \longrightarrow H^\bullet_{ads} \qquad [18]$$

$$CH_3{}^\bullet + H^\bullet_{ads} \longrightarrow CH_4 \qquad [19]$$

is formed by dimerization of the methyl radicals.

$$CH_3{}^\bullet + CH_3{}^\bullet \longrightarrow C_2H_6 \qquad [20]$$

Since the amount of ethane formed should be equal to that of hydrogen and that of CO_2 to the sum of methane plus twice the ethane evolved, the failure in the experimental observation of this stoichiometry suggests that other routes are responsible for the progress of the reaction and other organic intermediates, eg. ethanol and acetaldehyde, are produced and successively decomposed into CO_2 and H_2. In addition, evolution of methane is observed when hydrogen evolution is completely suppressed by preferential reduction of Pd^{2+}. This suggests that methyl radicals can abstract hydrogen from acetic acid (reaction 21). Finally, the parameters affecting the rate of

$$CH_3{}^\bullet + CH_3COOH \longrightarrow CH_4 + {}^\bullet CH_2COOH \qquad [21]$$

actic acid decomposition (illumination intensity and pH) indicate that ethane production becomes favoured as the rate of decomposition of acetic acid increases.

A recent report on the effect of pH and Ag^+ as the electron acceptor on the photocatalytic reactions of carboxylic acids in the presence of different powdered semiconductors allowed to put in evidence additional paths.[96] In alkaline media, only hydrogen is produced according to the reaction 22 ($\Delta G^o = 78.5$ kJ/mol). A reaction

$$CH_3COOH + 2H_2O \longrightarrow 2CO_2 + 4H_2 \qquad [22]$$

scheme of photocatalytic reactions of acetic in aqueous media is illustrated in Figure 10.

The same reaction on a dicarboxylic acid (eg. adipic acid) gave butane and CO_2 with lesser amounts of valeric acid and negligibly small quantities of oligomeric material.[97] The photodecomposition of benzoic acid gave however a mole ratio of CO_2 to benzoic acid consumed much larger than 1, suggesting that breakdown of the benzene ring must occur. The detection of salicylic acid in the experiments suggests the attack by OH• radicals on the benzene ring as a probable mechanism.

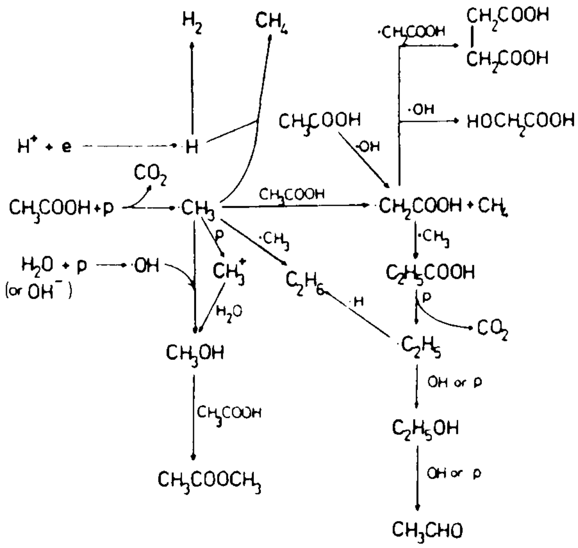


Figure 10 – Reaction scheme of photocatalytic reactions of acetic acid in aqueous media with powdered TiO_2 photocatalysts.

The photocatalytic process involving the simple polyfunctional carboxylic acid, levulinic acid, has been examined in the presence of TiO_2/Pt slurries.[98] The reaction is very complex and together with the expected decarboxylation route, other products have been

$$H_3C\text{-}CO\text{-}C_2H_4\text{-}COOH \xrightarrow[TiO_2/Pt]{hv} CH_3\text{-}CO\text{-}C_2H_5 + CO_2 \qquad [23]$$

found which probably originate by an initial C-C cleavage followed by decarboxylation. The distribution of organic products appears to be

$$\begin{tikzcd}
H_3C\text{-}CO\text{-}C_2H_4\text{-}COOH \arrow[r, "hv", "TiO_2/Pt"'] & H_3C\text{-}COOH \arrow[d, "TiO_2\ Pt"', "hv"] & + & H_3C\text{-}CH_2\text{-}COOH \arrow[d, "TiO_2\ Pt"', "hv"] & {[24]} \\
 & CH_4 + CO_2 & & C_2H_6 + CO_2 &
\end{tikzcd}$$

a very complex function of the crystallographic phase of TiO_2, level and method of platinization, surface area, pH and concentration of organic substrates. By selectively changing these parameters, it was possible to drive the reaction to the desired products.

Another semiconductor, α-Fe_2O_3, was reported to be active in the same reaction.[98] Decarboxylation of piruvic acid was investigated using CuO doped by univalent or trivalent ions, under visible light.[99]

5.5. Photoinduced Hydrogen Production from Biomass and Water

Possible photocatalytic processes for the non-biological conversion of materials derivable from biomass to a fuel and/or chemicals are of potential interest.

The photocatalytic reaction of glucose, the most common biomass building block, in the presence of TiO_2/RuO_2/Pt^{100} and TiO_2/$Pt^{101,102}$ gives H_2 and CO_2. The mechanism of the process presumably involves dehydrogenation of the hydroxy functional groups of the organic compounds and also of the aldehydes with formation of hydrogen and carboxylic acids. These last compunds are then available for decarboxylation via a photo-Kolbe reaction resulting in CO_2 evolution and a shorter chain alcohol which can continue to undergo oxidation. The end products are then only H_2 and CO_2. This process (and similarly for more complex carbohydrates) expressed in reaction 25, coupled with the photosynthetic process by green plants, equation 26, gives the total reaction 27 which is the water splitting reaction. Here

$$(C_6H_{12}O_6)_n + 6nH_2O \xrightarrow[\text{photocatalyst}]{h\nu} 6nCO_2 + 12nH_2 \quad [25]$$

$$6nCO_2 + 6nH_2O \xrightarrow[\text{green plants}]{h\nu} (C_6H_{12}O_6)_n + 6nO_2 \quad [26]$$

$$12nH_2O \longrightarrow 12nH_2 + 6nO_2 \quad [27]$$

$(C_6H_{12}O_6)_n$ represents glucose (n = 1), saccharose (n = 2), starch (n = ca. 100), and cellulose (n = 1000-5000) after hydrolysis. The quantum yields of the process decreases with increasing n.[101]

Moreover, various simple compounds are produced in addition to hydrogen. The photocatalytic decomposition of biomass is therefore similar to the fermentation process under anaerobic conditions, although it is carreid out in the absence of microorganisms and in a longer range of conditions (pH, temperature). Figure 11 reports a scheme of this semi-artificial cycle.

A large variety of other biomass sources, such as proteins, fats, and organic compounds in general, have been examined.[101] Since many of the organic products investigated are common waste products of biomass and of biomass processing industry, and inasmuch as these products are, in general, harmful to the environment and virtually impossible to separate from the aqueous phase, their photocatalytic conversion into H_2 and CO_2 (Na_2CO_3 or $NaHCO_3$, if carried out in NaOH solution) has much potential in cleaning up stream wastes providing simultaneously a clean fuel and useful chemical products.

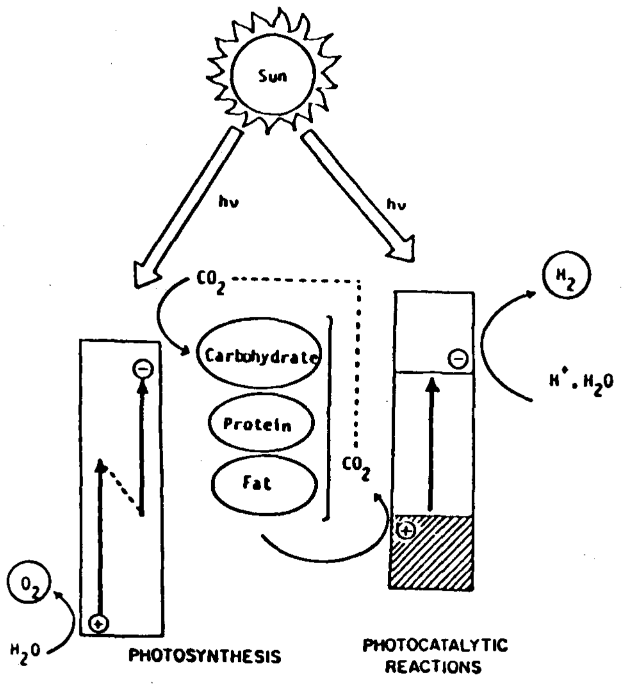


Figure 11 – Combination of the photocatalytic reactions with photosynthesis of green plants. The total reaction is water splitting.

6. PHOTOCATALYZED DEGRADATION OF WASTES

Heterogeneous photoassisted catalytic reactions of organic compounds have been reported in the preceding sections. Since some of the compounds are present as undesiable products in stream wastes, the possibility of using these processes in environmental control is desirable. Among other classes of compounds which present problems of environmental contamination, the organochlorinated derivatives and surfactant molecules are of paramount importance.

Until now, little attention has been devoted to heterogeneous photoassisted catalytic degradation of such compounds.[103] Only recently, degradation of halomethanes[104] and trichloroethylene[105] has been reported using illuminated TiO_2. Chlorophenols are totally mineralized into CO_2 and HCl, according to the overall reaction 28 (for pentachlorophenol) and the mass balance of chlorine-containing

$$HO\text{-}C_6Cl_5 + 4.5O_2 + 2H_2O \xrightarrow[TiO_2]{h\nu} 6CO_2 + 5HCl \quad [28]$$

organic compounds or other chlorine-containing derivatives.[106,107] The efficiency of different semiconductors is depicted in Figure 12. Oxygen and water were found to be essential to the reaction progress.

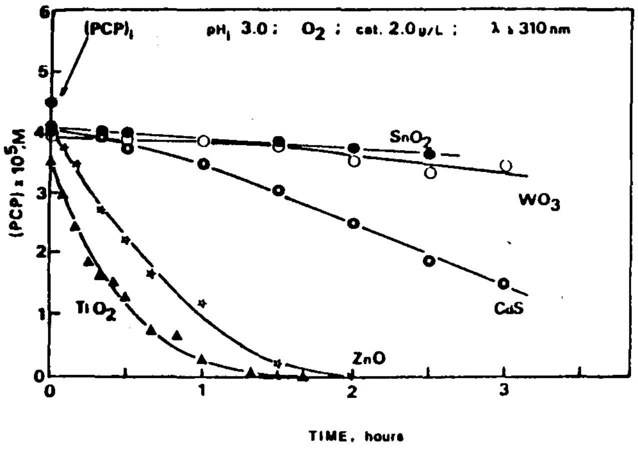


Figure 12 – Photodegradation of pentachlorophenol in the presence of various semiconductor disperions; wavelenght > 310 nm; initial [PCP] = 4.5 x 10^{-5}M; O_2 present; initial pH 3; unbuffered aqueous solutions; concentration of catalyst 2.0 g/l.

The application of the photodegradation processes is presently under investigation for a wide series of compunds also when present at very low concentrations.[108] In addition, experiments have demonstrated that the processes proceed at a significant rate also under direct sunlight (see Figure 13).[107] The problems originating from pollution by surfactant molecules are severe since the biodegradation of these compounds is often too slow and too inefficient.

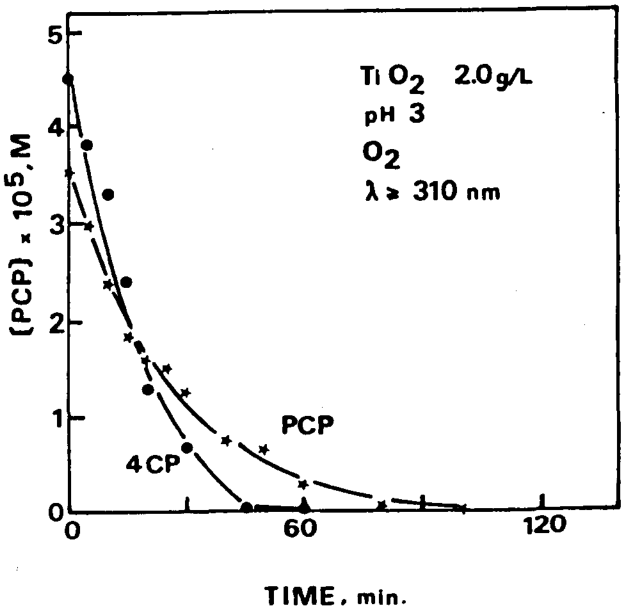


Figure 13 – Pentachlorophenol degradation under solar exposure in the presence of TiO_2 (2.0 g/l); date 17-7-1984; pH 3.0; O_2 present; initial [PCP] = 4.5 x 10^{-5} M; irradiation wavelengths > 300 nm; final [Cl^-] = 2.2 x 10^{-4}M; unbuffered dilute aquous solutions.

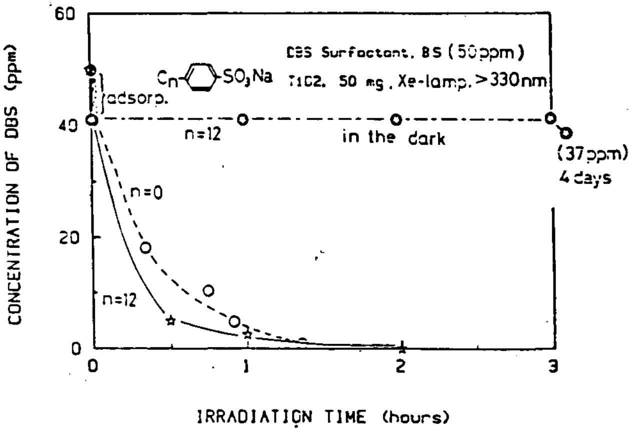


Figure 14 – Photodecomposition of n-dodecylbenze sulfonate (DBS) and benzene sulfonate (BS) in aqueous TiO_2 dispersions. The amount of DBS as calculated from its absorption at 224 nm is plotted as a function of irradiation time. Conditions: 50 mg of TiO_2, dispersed in 25 ml of neutral water, concentration of substrate is 50 mg/l.

The potential application of heterogeneous photodegradation has been demonstrated on the sodium dodecylbenzenesulfonate (DBS) in TiO_2, suspensions.[109] Figure 14 shows that the decomposition of DBS occurs efficiently (degradation of sodium benzenesulfonate is reported for comparison). Nuclear magnetic resonance studies and CO_2 determination suggest that the aromatic ring is first attacked by $OH^\bullet$ radicals and subsequently degrades.[110] Extension to other surfactants, including cationic and non-ionic surfactants is in progress.[111] It is also worthwhile noting that photocatalytic processes can be used for the oxidation of inorganic pollutants such as cyanide,[112,113] sulfite[112] (sulfides have been considered earlier in this work) and for the redox deposition of metal ions such as Cu^{2+} [114] and more important noble metals.[115]

7. CONCLUSIONS

Through suitable choice of materials, semiconductor powders coupled or uncoupled to suitable redox catlysts, allows desirable oxidation and reduction reactions to be performed under light irradiation. Together with the synthetic possibilities, two important fields, such as solar energy conversion and pollutant degradation, might benefit from an improvement of the performances and alteration of surface properties of semiconductor particulate catalysts via derivatization, sensitization, and increased stability.

In the short period, the cleavage of hydrogen sulfide, the dehydrogenation of alcohols, which are planned to be produced in significant amounts, and the decarboxylation of carboxylic acids, some of which are products of ermentation or of controlled degradation of cellulose or other biomass, represent useful routes to the manufacturing of clean fuels and useful chemicals. The possible application of the photoprocesses to the degradation of contaminants also can find a potential use. In fact, other degradation methods of pollutants are difficult to apply to water treatment inasmuch as microbial degradation and naturally occurring hydrolysis require long periods.

It thus appears that photocatalytic and photosynthetic processes on semiconductor powders are extermely promising in the solution of energy problems as well as in several other related fields; of importance is the degradation of contaminants whose increase appears exponential.

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REVISÃO

PRODUTOS NATURAIS DE ORGANISMOS MARINHOS

Uma revisão sobre os diterpenos da alga parda *Dictyota* spp.

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1. INTRODUÇÃO

Nos últimos quinze anos, o conhecimento sobre os compostos químicos de algas marinhas bentônicas tem aumentado enormemente. Tais organismos, pertencentes às divisões *Cyanophyta* (algas verde-azuladas), *Chlorophyta* (algas verdes), *Phaeophyta* (algas pardas) e *Rhodophyta* (algas vermelhas) apresentam um grande número de representantes produtores de metabólitos secundários, de ampla variedade estrutural, cuja maioria tem exibido, em laboratório, as mais diversas atividades biológicas. Os efeitos destes produtos em sistemas marinhos, no entanto, são ainda desconhecidos. Pesquisas recentes tem demonstrado que tais compostos fazem parte de uma estratégia presumivelmente defensiva frente a predação por herbívoros[1].

Existe vasta e considerável literatura toxicológica e química sobre os cianofíceas, principalmente da família *Oscillatoriaceae.* Foram caracterizadas lactonas macrocíclicas (e.g. debromoaplysiatoxina, (*1*) e alcalóides indólicos (e.g. lyngbyatoxina A, (*2*) que são apresentados no Quadro I. Informações detalhadas podem ser obtidas na excelente revisão de R. E. Moore[2].

Estudos mais limitados tem sido realizados sobre as algas verdes. Até o momento, a ordem *Siphonales,* típica de águas quentes, tem se revelado a principal produtora de compostos anti-herbívoros, cuja ação parece estar relacionada com a presença de diterpenos acíclicos contendo o grupo (E,E) 1,4-diacetoxibutadieno (e.g. 4,9-diacetoxiudoteal, (*3*)[3].

As algas vermelhas, em especial a classe *Florideophyceae,* foram intensamente estudadas. Em revisão recente, K.L. Erickson[4] comenta mais de duzentos e cinqüenta metabólitos secundários isolados somente do gênero *Laurencia*! Simplificando ao extremo, pode-se dizer que as algas vermelhas consistem no principal grupo de plantas marinhas produtoras de metabólitos polihalogenados, quer sejam terpenoidais (e.g. *4* e *5*) ou não (e.g. *6* a *8*).

Dentre as algas pardas, destacam-se os representantes da ordem *Dictyotales,* típicos de mares tropicais e subtropicais, sendo prolíficas na produção de substâncias fenólicas (e.g. *9*) e terpenoídicas (e.g. *10*).

Se a ação defensiva dos metabólitos secundários de macroalgas marinhas tem sido proposta, certamente nem todos os compostos isolados tem apresentado atividade anti-herbivoria. Alguns, tais como hidrocarbonetos odoríferos (e.g. *11*) conhecidos em vários gêneros de *Phaeophyceae,* estão envolvidos em outras funções vitais, atuando como ferormônios sexuais.[5]

Observações realizadas ao longo dos últimos anos tem demonstrado que os representantes tropicais e subtropicais são os principais produtores de compostos biologicamente ativos[1]. Espécies do mesmo gênero, porém de distribuição restrita às regiões frias não tem exibido tais propriedades, assim como outras espécies de águas quentes. Esta situação parece estar intimamente relacionada com diferentes estratégias evolutivas defensivas de macroalgas marinhas.

2. ESTRATÉGIAS EVOLUTIVAS DE ALGAS MARINHAS BENTÔNICAS E A SÍNTESE DE DEFESAS QUÍMICAS

Como mencionado acima, os metabólitos secundários mais abundantes das algas marinhas parecem estar relacio-